

## Percolation and conductivity: A computer study. II\*

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In this paper we present a large number of computer solutions of various types of resistor networks. Some of these are analogous to physical problems such as impurity conduction in lightly compensated semiconductors and variable-range hopping in amorphous semiconductors. A significant extension of the standard relaxation techniques was required to implement these solutions. The results of these calculations are compared to percolation-model predictions based on concepts developed in the first paper of this series. A simple criterion is found for the applicability of the critical-percolation-path analysis to problems of this type and this is used to formulate an accurate prediction for the impurity-conduction case. Arguments based on percolation models are also given to show that the  $T^{-1/4}$  and  $T^{-1/3}$  dependence of  $\log_{10}\sigma$  often predicted for three-dimensional and two-dimensional variable-range hopping are indeed expected to be observed, and results on resistivity networks analogous to these problems are shown to be consistent with these arguments. Accurate empirical formulas are deduced from these computer calculations and we use them to analyze some recent data on films of *a*-Ge. Employing the results of the preceding paper, several experimental studies, and our computer models we have also examined the utility of the critical-volume-fraction rule of Sher and Zallen in solving various types of mixture conduction problems. We find that application of this rule is appropriate only in rather limited circumstances, and that in general a knowledge of the topological properties of these problems must be employed in finding the percolation threshold.

### I. INTRODUCTION

In the preceding paper<sup>1</sup> (I) we discussed many percolation models, several of which we shall show are appropriate to the solution of problems dealing with hopping conduction. The basic conclusion was that the percolation problems posed on a random lattice were sufficiently varied and complex that no known simple procedure or rule of thumb could be universally applied to yield accurate answers. The alternative method of empirical solution via computer or other methods was offered as a practical alternative to theoretical techniques. In this paper (II) we will compare some of the percolation solutions obtained in paper I via Monte Carlo methods to the computed conductivity of actual resistor networks.<sup>2</sup> The computational methods required to solve these networks will be discussed and the solutions will be compared to the relevant percolation models in order to deduce criteria for applicability of percolation theory to problems of this type.

The detailed plan of the paper is as follows: In Sec. II we will describe the results of solving for the conductance of a simple cubic lattice with conductances joining nearest-neighbor nodes. The results for this case will be seen to suggest a simple test for the applicability of percolation theory. In Sec. III we solve for the conductivity of a random lattice with conductances depending exponentially on the distance between nodes. These results are compared to the percolation results of paper I. We generalize this problem in Sec. IV by assigning random energies to the lattice nodes of the preceding case and solve for the conductance of the net-

work in the case where the conductance between sites is given by the Miller-Abrahams<sup>3</sup> (MA) formula. The empirical results for two- and three-dimensional networks yield accurate empirical formulas characterizing variable range hopping in both cases. These formulas are compared to the theoretical results of Mott,<sup>4</sup> Pollak,<sup>5</sup> and Ambegaokar *et al.*<sup>6</sup> Section V is a brief discussion of the available experimental results on conduction in mixtures of insulating and metallic phases with reference to the percolation concepts which have been applied to these problems. Section VI summarizes the results of paper II.

### II. SIMPLE CUBIC LATTICE CONDUCTANCE NETWORK

The case of a simple cubic (sc) lattice of nodes with conductances joining nearest neighbors has been considered previously by Kirkpatrick.<sup>7</sup> We will review and extend his treatment because it provides a clearcut demonstration of when certain results from percolation theory can be expected to *accurately* predict some of the conductance properties of these networks. In the present case we have investigated the conductivity of such networks when the individual conductances between the *i*th and *j*th nodes,  $G_{ij}$ , are chosen to have their logarithms uniformly distributed between  $\log A$  and  $-\log A$  (preserving Kirkpatrick's notation). While Kirkpatrick limited his study to values of  $A$  below  $10^3$ , we have allowed  $A$  to range up to  $10^7$ . We note as have Ambegaokar *et al.*<sup>6</sup> that percolation theory must give exact results in the asymptotic ( $A \rightarrow \infty$ ) limit; our purpose here is to determine how large

$A$  must be before the percolation predictions become sufficiently accurate to apply them to physically useful situations.

The application of percolation concepts to this problem is straightforward. One construction, due to Ambegaokar, Halperin, and Langer<sup>6</sup> (AHL), which provides a lower bound to the conductivity is to place the conductances on the lattice in order of their values starting with the largest and stopping when the first path opens across an infinite sample. The smallest conductance in this subnetwork will hereafter be called the critical conductance,  $G_c$ . We can set a lower bound weaker than that provided by the AHL construction if we replace all the conductances on the AHL subnetwork by  $G_c$ ; this construction has the advantage of making the dependence of the network conductivity on  $A$  transparent. For this reason we shall make consistent use of this lower bound network. This simple application of percolation theory provides us only with information about the  $A$  dependence of the conductivity; however, as we shall show later, this type of information is sufficient to give us the temperature dependence of the conductivity in the case of problems involving hopping conduction.

To deduce the  $A$  dependence of the lower bound network we have only to find  $G_c$ . Monte Carlo studies of probabilistic bond percolation on this lattice<sup>8</sup> have shown the critical bond fraction  $p_{b,c} \approx 0.25$ . If we put the individual conductances  $G_{ij}$  into the lower bound network, largest first, the critical conductance occurs when  $\frac{1}{4}$  of the  $G_{ij}$ 's have been inserted: therefore,  $\log G_c = \frac{1}{2} \log A$ . Thus this simple percolation model predicts that  $\partial \log \sigma / \partial \log A = \frac{1}{2}$ .

The actual conductivity of these simple cubic networks was calculated with the aid of a CDC-6600 computer using samples of 1000 nodes each. All node-to-node conductances between  $1/A$  and  $A$  were randomly assigned. The voltage of one surface plane on the  $10 \times 10 \times 10$  array<sup>9</sup> was fixed at 1 V and the voltage on the opposite face was set at zero; the voltage of the nodes on the other four surface planes parallel to the applied field was allowed to float, determined only by the current flowing into them via their five nearest-neighbor conductances. The initial algorithm used reset the voltage of each node in turn so that the total current into that node was made to vanish. The deviation from zero of the current into each node was monitored as well as the current into and out of both fixed-voltage surface planes. The network was considered solved when the currents in and out of each end coincided, and the average nodal current deviation became vanishingly small. When the conductance-spread parameter  $A$  exceeded  $\sim 10^3$ , this algorithm required an excessive number of iterations to achieve the solution. We then examined the de-

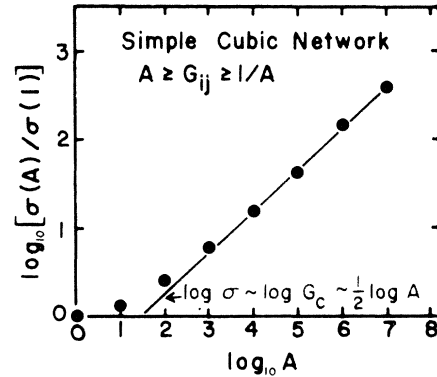


FIG. 1. Conductivity of a simple cubic network as a function of conductance spread. The circles denote computed conductivities (normalized by the value at  $A=1$ ) of simple cubic networks whose intersite conductances  $G_{ij}$  are uniformly spread (on a logarithmic scale) between  $1/A$  and  $A$ . The solid straight line is the predicted variation from a critical path analysis.

tailed node voltages for large  $A$  and found that a sizable fraction of them were almost identical. This, as we shall see later, is a natural consequence of the percolative tendencies of these networks. Since the simple iterative scheme can be shown algebraically to become very inefficient under these conditions, a cluster iteration approach was devised (see Appendix A). This approach allowed us to solve the networks in the large  $A$  regime using practical amounts of computation time.

The results of these computations are shown in Fig. 1. Here we have plotted the computed 1000-node-network conductivity for various values of  $A$ , normalized by the conductivity when  $A=1$  (all  $G_{ij}$ 's = 1 mho). Each point above  $A \approx 10^2$  is the geometric average of  $\sim 10$ – $12$  different individual networks. Numerous samples were required because of the scatter inherent in computations on finite size samples. The solid line in Fig. 1 is the variation predicted using the simple lower bound network. It is clear that for  $A \lesssim 10^3$  the predictions of the percolation model are not particularly useful in characterizing these networks, but as Kirkpatrick<sup>7</sup> stated, an effective medium theory can be useful in this regime. Above  $A \approx 10^3$ – $10^4$  the experimental points do follow closely the slope ( $\frac{1}{2}$ ) of the solid line.<sup>10</sup> This agreement with the percolation theoretical prediction implies that the first paths opening up across the network are the crucial ones, provided that the conductance spread is at least this large. We shall see later that this conductance-spread condition is satisfied in the real physical problems discussed in Secs. III and IV; thus, we should expect the percolation analysis of these situations to be usefully accurate.

We have also solved some of these sc networks

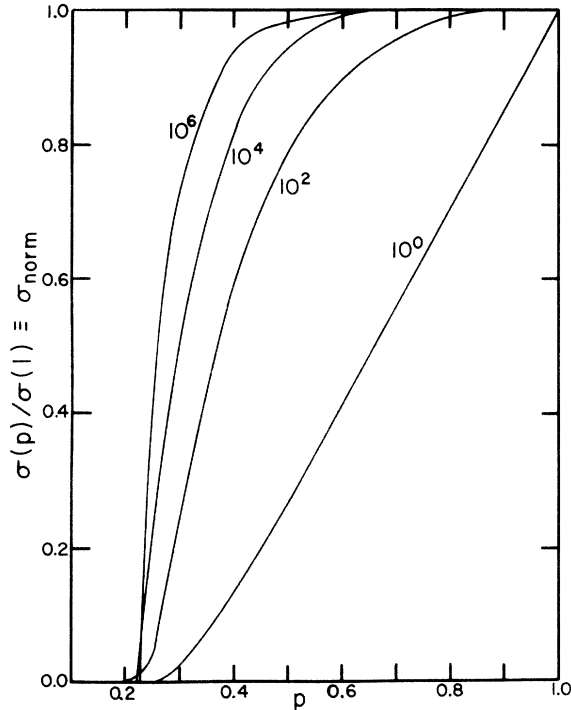


FIG. 2. Computed conductivities of several simple cubic networks versus the fraction  $p$  of conductances present in the networks. All networks had values of the individual conductances  $G_{ij}$  ranging from  $A$  to  $A^{1-2p}$ , with the value of  $A$  being indicated on each curve. All conductances are normalized by the completed network ( $p = 1$ ) values.

as a function of  $p$ , the fraction of conductances present in the lattice, where the conductances are inserted into the network in AHL fashion, largest first. The results, shown in Figs. 2 and 3, indicate that the conductance paths opening up after the first percolation paths (at  $p = 0.25$ ), although less tortuous, make minimal contributions to the filled network conductivity when  $A$  is  $> 10^3 - 10^4$ . These results imply that the so-called directional constraints used by MA<sup>3</sup> and Pollak<sup>5</sup> to effectively restrict the current paths to the forward direction (in the direction of the applied field) appear to be superfluous.

### III. IMPURITY CONDUCTION AT LOW COMPENSATION

In lightly doped crystalline semiconductors at low temperatures, carrier transport is by hopping conduction. Miller and Abrahams<sup>3</sup> have shown that electrically this situation may be represented by a network of conductances. The nodes of this network are spatially at the randomly located impurity sites, and the value of individual node-to-node conductances depends in general on the site separation and the site energies. At small compensation

ratios most of the majority impurity sites have nearly the same energy, and hence the intersite separation dominates the individual node-to-node conductances.

As in the simple cubic network case, we consider finding the critical conductance  $G_c$ , which forms the first chain of infinite extent by placing conductances into the random lattice, largest first. The individual conductances, due to carrier wave-function overlap, are given by<sup>3</sup>

$$G_{ij} = G_0 \exp(-2d_{ij}/a), \quad (1)$$

where  $d_{ij}$  is the distance between nodes  $i$  and  $j$  and where  $a$  is the radius of the localized wave function. In this case we shall find that application of the simple lower bound construct leads to a prediction of the impurity density dependence of the network conductivity. Finding the critical conductance is equivalent to finding the critical size of OLF's (overlapping figures; in this case, spheres) centered about each node of the network. The critical percolation radius of these spheres was found in paper I to be,  $r_c \approx 0.7(3/4\pi N_s)^{1/3}$ ; thus  $G_c$  is found to be the conductance connecting two impurities a

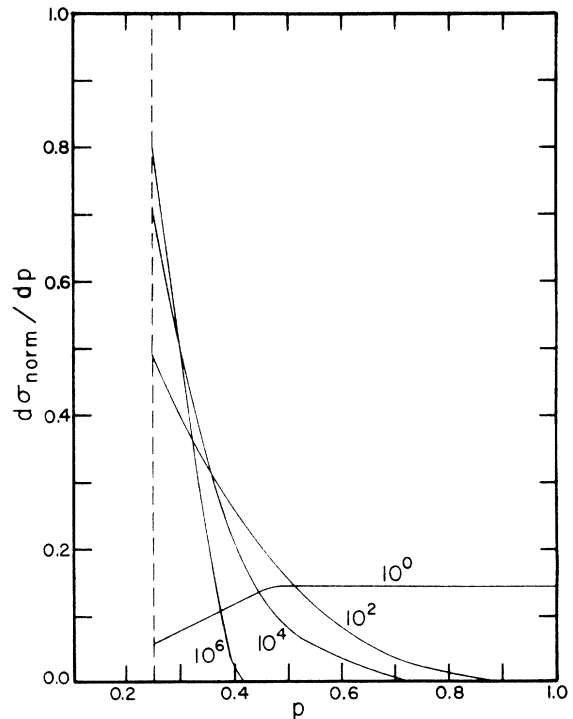


FIG. 3. The derivatives of the curves shown in Fig. 2 with respect to  $p$ . These curves are the change in the network conductivity per unit increment in the fraction  $p$  of intersite conductances. For large  $A$  they become sharply peaked near the critical bond fraction 0.25, indicating that a critical path analysis is very useful in this regime.

distance  $2r_c$  apart. Using Eq. (1) the dependence of the lower bound network conductivity on node density  $N_s$  is given by

$$\sigma \propto \exp[-(1.4)(2/a)(3/4\pi N_s)^{1/3}] . \quad (2)$$

To test this prediction, we have solved for the conductivity of a large number of 1000-node random networks of different density using internode conductances determined by Eq. (1). These networks were computer-solved using techniques elaborated upon in Sec. II. The situation is somewhat more complicated in this case because each point of the computer-generated network must be assigned a random spatial position. Once this was accomplished it remained only to establish how many conductances out of each node were truly important (i. e., carried the majority of the current). By solving the networks while including only the  $n$  largest conductances originating from each node, it was empirically determined that  $\sigma$  was rather independent of  $n$  beyond  $n = 5$  or  $6$ . In actual practice  $n$  was allowed to range from 10 to 15. The boundary conditions imposed on these random networks were as follows: the voltage of all points within a certain fraction (usually  $\sim 0.05$ ) of one end of the network was set at zero, whereas the voltage of all the nodes lying within that same fraction of the other end was fixed at 1 V. The voltage of all other nodes was externally unconstrained. The cluster iteration algorithm used for the sc lattice networks was employed with the average nodal current deviation being monitored as well as the currents into and out of each fixed voltage region.

The solved network conductivities obtained from these calculations are shown in Fig. 4. The wave-function radius  $a$  was arbitrarily chosen to be  $15 \text{ \AA}$  and the spatial site densities range from  $3 \times 10^{16}$  to  $10^{19} \text{ cm}^{-3}$ ; the points are actually plotted versus twice the "average" site separation,  $\bar{r}_s = (3/4\pi N_s)^{1/3}$ , divided by  $a$  for easy comparison with the percolation prediction. Each data point is the average of about 10 separate network calculations. The line drawn as a best fit through the data has a slope of 1.39, remarkably close to the lower bound network prediction of 1.4.<sup>11</sup> A computer printout of the 10 largest conductances from each node revealed that these were, except for the highest density employed, spread over a range of at least  $10^6$ ; the excellent fit of all but the  $N = 10^{19} \text{ cm}^{-3}$  point to the solid line in Fig. 4 is therefore consistent with the conclusions drawn from the sc lattice case concerning the region of applicability of the lower bound construct.

Now that we have a theoretical prediction for the behavior of these "R-percolation" networks, as Pollak<sup>5</sup> calls them, we can examine the impurity conduction data of Fritzsche and Cuevas.<sup>12</sup> Pollak<sup>5</sup> has shown that their data have the  $N_s$  dependence

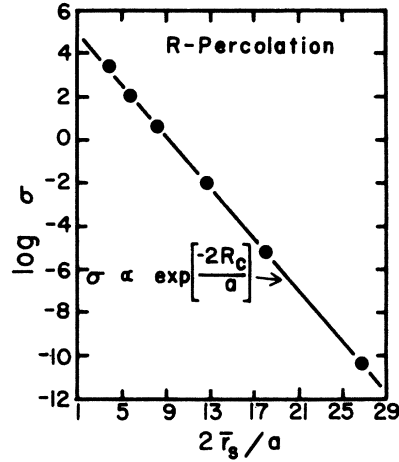


FIG. 4. Impurity conduction in the  $R$ -percolation limit. The circles denote the computed conductivity of a random lattice of sites interconnected by conductances whose value depends exponentially on the intersite separation and the wave-function radius  $a$ . The straight line is the percolation theoretical prediction for a low compensation ratio.

predicted by Eq. (2); using the slope deduced from Fig. 5(P) in his paper,<sup>5</sup> we deduce that  $a = 72 \text{ \AA}$  for low compensation in Ga doped Ge. This should be compared with the value of  $62 \text{ \AA}$  deduced by Pollak<sup>5</sup> using his lower bound estimate of the critical sphere percolation radius. Miller and Abrahams<sup>3</sup> deduce a value of  $90 \text{ \AA}$  for  $a$ , but their formulation is not based on a true percolation model and gives a prediction for the density dependence of  $\sigma$  which is not particularly consistent with that displayed by the data. We note here that there is agreement between the value of the wave-function radius deduced by us and Golin's estimate<sup>13</sup> of  $75 \text{ \AA}$  obtained from ac conductivity experiments.

#### IV. VARIABLE-RANGE HOPPING

We have demonstrated in Sec. III that computer analyses of spatially random resistor networks are feasible. To simulate the variable-range hopping problem we now have only to assign energies to our sites and include a suitable energy dependence of the intersite conductance. For our actual conductivity computations we used the full MA formula [Eq. (III-9) of Ref. 3]. However, for ease of discussion we use an approximate form due to AHL,<sup>6</sup>

$$G_{ij} = G_0 \exp\left(-\frac{2d_{ij}}{a} - \frac{|E_i| + |E_j| + |E_i - E_j|}{2kT}\right) \\ \equiv G_0 e^{-t} \quad (3)$$

where  $d_{ij}$  and  $a$  are the same as for Eq. (1) and  $E_i$  and  $E_j$  are the energies of carriers on sites  $i$

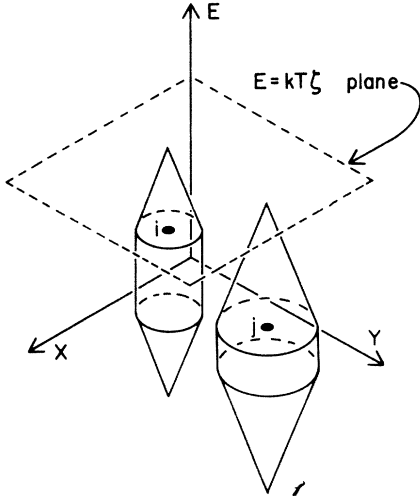


FIG. 5. The shells of constant  $\xi$  [Eq. (3)] for two arbitrary sites  $i$  and  $j$  in an IF construction simulating variable-range hopping conductivity in two spacial dimensions. Here the  $x$  and  $y$  coordinates of the sites correspond to the real spatial positions of  $i$ th and  $j$ th localized states and the height of any point above the  $xy$  plane is the energy of that state. If any other point  $k$  (not pictured here) lies within the shell about  $i$ , then  $\log G_{ik} < \xi$ . In the associated percolation model all sites lying within the shell about  $i$  are considered bonded to  $i$ . The percolation threshold needed for a critical path analysis is found by expanding the shells (increasing  $\xi$ ) until an infinite cluster of bonded sites occurs. Dimensions of these shells are given in text.

and  $j$ . Rather than dwell at length on the appropriateness of Eq. (3) to certain applications such as electron hopping in  $\alpha$ -Ge, it suffices to mention that the general form of this result, a tunneling overlap plus an intersite energy difference term, is to be expected for a wide variety of quantum tunneling processes.<sup>6</sup> Before turning to the details of the computer-solved networks for this problem, we will first discuss the geometrical percolation problem relevant to this case. A discussion of the approximate models used by several authors to deduce the conductivity will be deferred until later in this section.

For analytical purposes it would be useful to have a geometric percolation model for the two-dimensional (2D) and three-dimensional (3D) variable-range hopping problem. Then the results of paper I pertaining to percolation "invariants" could be used. Unfortunately, one cannot construct a set of overlapping figures having a one-to-one correspondence between overlap or nonoverlap of figures and the occurrence or nonoccurrence of bonds. We can, however, construct inclusive figures (IF's) and apply the critical-number-of-bonds-per-site technique. The IF construction that we will employ results from considering the site energy to be an ad-

ditional dimension. In Fig. 5 we demonstrate this concept (for the 2D problem) by drawing the surfaces of constant conductance [from Eq. (3)] associated with two arbitrary, unconnected nodes. In this form this is a site percolation problem since any node which lies within the surface of node  $i$  is connected to node  $i$ , and likewise for node  $j$ . A similar construction can be made in four space to simulate the 3D variable-range hopping problem, but this obviously is harder to visualize, and we shall confine ourselves here to calculations involving the model in Fig. 5 appropriate to the 2D problem. Using the definition of  $\xi$  in Eq. (3), we note that the shells of constant impedance about site  $i$  consist of three sections: a cylinder of height  $E_i$  (measured from the Fermi energy) and radius  $R_i = a/2(\xi - E_i/kT)$ ; at both ends this cylinder is capped by a right cone of the same radius whose height is  $kT\xi - E_i$ .

A solution to this conductivity problem can be found (assuming the validity of the critical path analysis) by deducing the critical value  $\xi_c$  of the conductance exponent in Eq. (3) at which we have just completed a path of bonds across an infinite sample. This is equivalent to finding the size of the constant conductance shells in Fig. 5 at their percolation threshold. From the dimensions given above we can calculate the volume enclosed by the shell about site  $i$ . We find

$$V_i = \frac{\pi a^2 kT}{12} \left\{ 2\xi^3 - \left[ \left( \frac{3}{kT} \right) \xi^2 E_i \right] + \frac{E_i^3}{(kT)^3} \right\}. \quad (4)$$

It is now trivial to compute the average volume of all the sites having energies lying between  $\pm \xi kT$ ; this quantity,  $\bar{V}$ , when multiplied by  $N$ , the density of states (assumed constant in energy here), yields  $\bar{B}$ , the average number of bonds per site. Thus

$$\bar{B} = N\bar{V} = \frac{1}{16} \pi a^2 kTN \xi^3. \quad (5)$$

Inverting this, we have for the critical exponent

$$\xi_c = C_2 (a^2 kTN)^{-1/3}, \quad (6)$$

where

$$C_2 = (16\bar{B}_c/\pi)^{1/3}.$$

From Eq. (6) we can see that if  $\bar{B}_c$  is not a function of  $N$  or  $T$ , the critical path analysis predicts the familiar  $T^{-1/3}$  formula for 2D variable-range hopping.<sup>14</sup> Analogous arguments can be made in the 3D case to show that the  $T^{-1/4}$  formula will result if the average number of bonds per site at percolation remains constant with variations of  $N$  and  $T$ . These yield

$$\xi_c = C_3 (a^3 kTN)^{-1/4}, \quad (7)$$

where

$$C_3 = (40\bar{B}_c/\pi)^{1/4}.$$

As shown in paper I, the average number of bonds per site at percolation is not a dimensional invariant. Hence, for this model, we have no means of obtaining an accurate value of  $\bar{B}_c$ . However, we do prove in Appendix B that, whatever its true value,  $\bar{B}_c$  is independent of  $N$  and  $T$ . Therefore the  $T^{-1/3}$  and  $T^{-1/4}$  laws are closely obeyed if Eq. (3) exactly describes the internode conductance and if we have sufficient conductance spread to guarantee that the percolation analysis of the network is accurate.

One way to obtain rough estimates for  $C_2$  and  $C_3$  would be to use the values obtained for  $\bar{B}_c$  in representative percolation problems involving IF's percolating in 3 and 4 space, respectively. Taking the 3-space value of 2.8 bonds per site obtained for random-lattice percolation of spheres (Table III of paper I), Eqs. (6) and (7) yield  $C_2 = (16\bar{B}_c/\pi)^{1/3} = 2.42$ , a number that we will find to be within 20% of the observed value later in this section. Likewise, using the 4-space value of  $\bar{B}_c = 2.11$  for hyperspheres,<sup>1</sup> we calculate  $C_3 = (40\bar{B}_c/\pi)^{1/4} = 2.28$  as a rough estimate.

The percolation models based on the AHL conductance formula, Eq. (3), are already complex. Models based on the full MA form with its Fermi functions and exponential prefactors are nearly intractable. For this reason we feel that a computer simulation may be the only approach to the problem likely to yield a reasonably accurate prediction for variable range hopping conductivity. Towards this end we have solved a large number of 500- to 1000-node conductance networks using a variety of temperatures in the MA formula. The data obtained span a range of 30 decades in conductivity and thus allow predicted power law dependences such as  $T^{-1/4}$  to be determined. The density of states in energy used for both the two-dimensional and three-dimensional studies is shown in Fig. 6(b). It is constant in energy and symmetric about the Fermi level with a width of 10 meV. Three total (spatial) densities of states were chosen for the 3D case:  $10^{17}$ ,  $10^{18}$ , and  $10^{19}$  cm<sup>-3</sup>. For the 2D case we chose  $N_s = (10^{18} \text{ cm}^{-3})^{2/3}$  to correspond to the thin film (thickness  $\leq r_{\text{hop}}$ ) behavior of the  $10^{18} \text{ cm}^{-3}$  3D case. For all studies the wavefunction radius was arbitrarily chosen to be  $a = 15$  Å. The temperatures used for both cases ranged from 0.2 to 80 K. Methods used for setting up and solving the networks were identical to those elaborated upon in Secs. II and III.

The conductivity results for the three-dimensional networks are shown in Fig. 6(a). Each point is the appropriate average<sup>15</sup> of some 10 to 15 different network solutions. It should first be noted that the high temperature ( $kT \gg 2\eta$ , where  $\eta$  is the width in energy of the density of states) behavior of  $\sigma$  is not consistent with a power law dependence

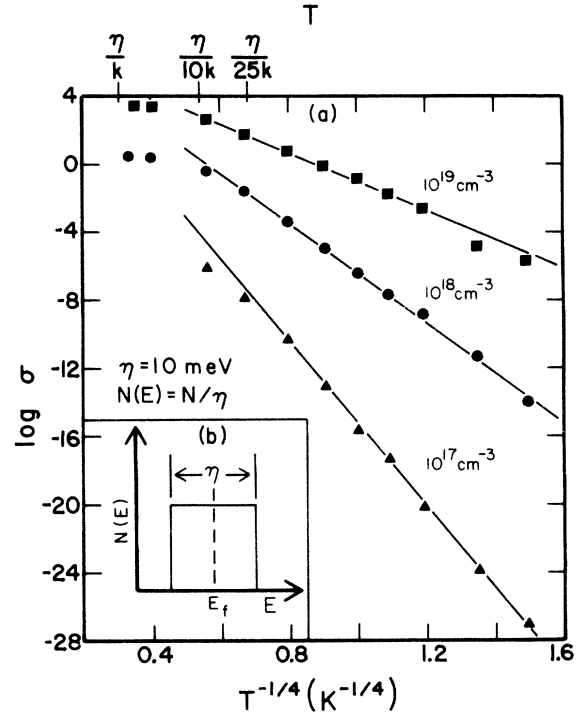


FIG. 6. Variable-range hopping conductivity in 3D. The data points shown here denote the computed conductivity of a 3D random lattice of sites interconnected by conductances of the MA form. For nearly all the plotted data, the data point symbol is much larger than the uncertainty of the value (Ref. 15). The sites have randomly assigned energies between  $\pm 5$  meV of the Fermi level  $E_F$ . The curves are best-fit straight lines to a  $T^{-1/4}$  dependence for low  $T$ . The upper abscissa scale shows a few important values of  $T$  in terms of the density-of-states width  $\eta$  over the Boltzmann constant  $k$ .

of  $\log \sigma$  upon  $T$ ; as we shall discuss later, this deviation is not unexpected and has been predicted by Pollak *et al.*<sup>16</sup> The low-temperature data at each density were trial fitted to a number of different power law dependences (i. e.,  $\log \sigma \propto T^{1/3}$ ,  $T^{1/3.5}$ ,  $T^{1/4}$ , etc.). Due to the scatter in the data it was not possible to say precisely (to within better than  $\sim \pm 10\%$ ) which value of the exponent was the best for each site density although there were definite indications from least-squares analyses that the best-fit exponent was somewhat larger than  $\frac{1}{4}$ . For comparison with theory, we plotted all the data versus  $T^{-1/4}$ . The experimentally determined slopes of  $\log \sigma$  vs  $T^{-1/4}$  are presented in the upper part of Table I. Here we have given them in terms of the combination,  $[a^3 N(E) k]^{-1/4}$ , for ease of comparison with our theoretical predictions and those of Mott,<sup>4</sup> AHL,<sup>6</sup> Pollak,<sup>5</sup> and Jones and Schaich.<sup>17</sup> It can be seen that our "experimental" values of  $C_3$  are typically 20% larger than all but the first of these theoretical predictions and are *not* strictly

TABLE I. Coefficients in the conductivity exponent.  $C_3$  and  $C_2$  are given by  $\sigma_{3D} = \sigma_3 \exp\{-C_3[a^3 N(E)kT]^{-1/4}\}$ ,  $\sigma_{2D} = \sigma_2 \exp\{-C_2[a^2 N(E)kT]^{-1/3}\}$ .

	$N(E)$	Computer results <sup>a</sup>	This paper <sup>b</sup>	Mott <sup>c</sup>	Pollak <sup>d</sup>	AHL <sup>e</sup>	Jones and Schaich <sup>f</sup>
$C_3$	$10^{21}$	$2.60 \pm 0.09$					
	$10^{20}$	$2.48 \pm 0.06$	2.28	2.05	1.84	2.00	1.78
3D	$10^{19}$	$2.31 \pm 0.04$					
$C_2$	$10^{14}$	$2.21 \pm 0.08$	2.42	2.05	1.74	2.00	...
	2D						

<sup>a</sup>Maschke, Overhof, and Thomas (Ref. 17) have recently made two-dimensional computer calculations similar to ours. They find an exact  $T^{-1/3}$  behavior with  $C_2$  between 2.49 and 2.66. However, they use the purely exponential (AHL) form for the individual conductances.

<sup>b</sup>The values given in this column are the estimates derived in Sec. IV assuming constant values for  $\bar{B}_c$  obtained from the percolation of spheres (for  $C_2$ ) and hyperspheres (for  $C_3$ ).

<sup>c</sup>Reference 4.

<sup>d</sup>Reference 5.

<sup>e</sup>Reference 6.

<sup>f</sup>Reference 17.

constant with changing  $N$ . This variation of  $C_3$  is larger than the uncertainty of the slopes determined from the data in Fig. 6(a). This fact, taken together with the above-mentioned deviation of the best-fit power law dependence from  $T^{-1/4}$ , indicates that this law is closely but not exactly obeyed.

The failure of the data to precisely fit a  $T^{-1/4}$  law could be the result of several factors. The first is that a critical path analysis may not be sufficiently accurate due to an inadequately wide spread of the three to six largest impedances from each site. This appears unlikely, however, since the  $R$ -percolation data [which are the high- $T$  limits of each curve in Fig. 6(a)] for all but the highest density appear to accurately follow the critical path predictions. For all practical purposes, then, we are in the region where the percolation predictions are very good indeed. These deviations are most likely the result of the fact that the MA form of the impedances used here is not strictly in exponential (AHL) form but contains preexponential factors dependent on  $\gamma_{ij}$  and  $T$ . Inclusion of these factors into a theoretical treatment of the problem makes the situation rather intractable, but a reasonable estimate is that the first-order corrections obtained from taking these factors into account should be small. Indeed we have found that a rather mild preexponential to the derived  $\exp(-T^{-1/4})$  equation (of the form  $T^{1/2}$ ) is sufficient to explain our observed "experimental" deviations.<sup>18</sup>

It is now useful to briefly interrupt our examination of the data in order to review prior derivations

of the theory of variable-range hopping conductivity. We will confine ourselves to discussing the treatments which have occurred after the initial suggestions of Mott.<sup>4</sup> Mott was the first to recognize the variable-range aspect of the problem but at the time made only qualitative estimates of the behavior expected in this situation. Pollak<sup>5</sup> has attempted to solve the percolation aspect of this problem by evaluating the onset of percolation using a formula for the expectation value of the number of paths of length  $N$  steps, all of which consist of impedances less than some value  $Z$ . This formula provides only a lower bound to the percolation threshold, however, since its stochastic nature necessarily implies that it overestimates the expectation value due to its inclusion of multiply re-traced paths. The fact that this is an approximation has been recognized by Pollak<sup>5</sup> and others. Some estimate of how far off this estimate might be can be made by considering the  $R$ -percolation problem (Sec. III) (see Ref. 23 of paper I): Pollak's formulation can be evaluated exactly in this case and yields  $R_c = \bar{\gamma}_s$  while the actual value (Table III of paper I) is  $R_c = 1.4\bar{\gamma}_s$ . We are therefore not surprised that our values of  $C_3$  are about 25% higher than his.

Ambegaokar, Halperin, and Langer<sup>6</sup> have also applied percolation theory to this problem. However, both of their percolation models involve the percolation of variable-sized spheres in 3-space. Thus their models do not possess a one-to-one correlation of bonds made and figures overlapping (or points included in the case of their first model).

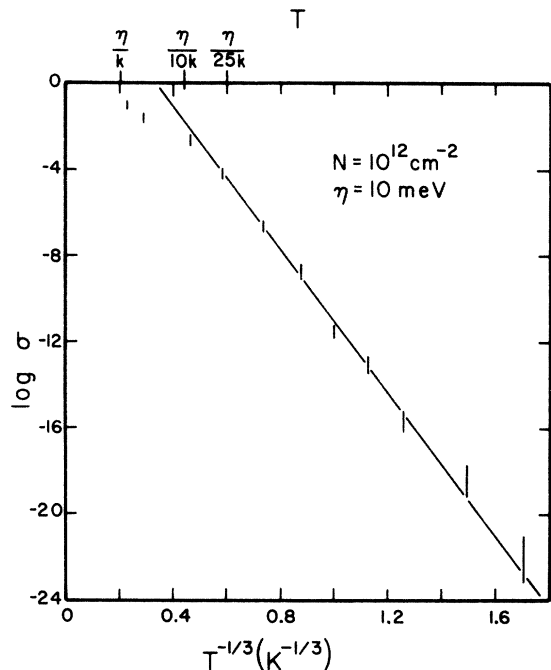


FIG. 7. Variable-range hopping conductivity in 2D. The bars denote the computed conductivity of a 2D random lattice of sites interconnected by conductances of the MA form. Site energies are assigned as in 3D. The curve is a best-fit line to a  $T^{-1/3}$  dependence at low  $T$ .

We must thus conclude that their value of  $C_3$  should be regarded as a rough estimate. On this basis their value of  $C_3 = 2.00$  appears to be in good agreement with our data. The work of Jones and Schaich<sup>17</sup> also involves estimates of percolation models which are not exact simulations to the conduction problems; their estimate of  $C_3$  is 1.78. Before leaving our discussion of the low-temperature section of the data in Fig. 6(a), we should remind the reader that a desire for a precise value of  $C_3$  is not merely an academic point: any errors in  $C_3$  are magnified to the fourth power in a determination of the wave-function radius or the density of states from empirical data.

Turning to the high-temperature regime, the breakover seen in the data in Fig. 6 is a result of the fact that the temperature-dependent part of the exponent in Eq. (3) becomes negligible. Thus the variable range aspect of the problem disappears at large  $T$ , and the hopping processes enter the “ $R$ -percolation” regime discussed in Sec. III. Our indications of when this occurs in temperature agree roughly with the theoretical estimates of Pollak *et al.*<sup>16</sup>: We therefore concur with their contention that the observance of  $T^{-1/4}$  behavior up to relatively high temperature (in their case  $\sim 200$  K) is consistent with reasonably narrow widths of state

densities about the Fermi level (their estimate is  $\sim 0.1$ – $0.3$  eV for  $a$ -Ge).

The conductivity results for the two-dimensional networks are shown in Fig. 7 for a spatial site density of  $10^{12}$   $\text{cm}^{-2}$ . The energy dependence of  $N(E)$  is identical to that used in the 3D case [Fig. 6(b)]. Due to the limited amount of data, we have not performed any analyses to determine the best-fit power law dependence for the low- $T$  data. Instead we have chosen a  $T^{-1/3}$  scale for the abscissa in line with theoretical considerations: it can be seen that this provides a reasonable fit to the data. Knotek *et al.*<sup>14</sup> have applied the formulations of Mott,<sup>4</sup> Pollak,<sup>5</sup> and AHL<sup>6</sup> for the case of two dimensions with the formula shown at the bottom of Table I resulting in each case. The constant  $C_2$  obtained for each treatment is shown in the lower half of Table I along with the present, empirically determined, result deduced from the slope of the data in Fig. 7. We note again that as in the 3D case the flattening of  $\log \sigma$  vs  $T^{-1/3}$  at high  $T$  is the result of the transition to the temperature independent “ $R$ -percolation” regime.

We feel that the present calculations should serve as a reasonably reliable basis for evaluating conductivity data where variable-range hopping is suspected. As an example we will apply the 2D and 3D formulas listed in Table I to the data of Knotek *et al.*<sup>14</sup> on “thin” and “thick” films of  $a$ -Ge. These conductivity data display a transition from  $T^{-1/4}$  to  $T^{-1/3}$  behavior as the film thickness drops below  $\sim 400$  Å. If we make the rather crude assumptions that the wave-function radius and density of states are independent of sample thickness we can deduce both  $a$  and  $N(E)$  from their experimental data. Using the formulas in Table I we obtain a  $\approx 17$  Å and  $N(E) \approx 3 \times 10^{16}$   $\text{cm}^{-3} \text{eV}^{-1}$ . These numbers should be compared to the values of  $\sim 10$  Å and  $2 \times 10^{17}$   $\text{cm}^{-3} \text{eV}^{-1}$  that they obtained using Pollak’s<sup>5</sup> theory. Our result suggests fewer states in the gap, thus pushing the transport estimate of  $N$  far below the upper limit of the number of gap states estimated from optical absorption data. Hence, it appears that the present study enhances the possibility that low-temperature transport in  $a$ -Ge may be an example of true variable-range hopping conduction.

## V. CONDUCTION IN MIXTURES

There are a variety of problems concerned with electrical conduction in two component mixtures. In the case where the conductivity of one of the components is very much larger than that of the other, knowledge of the composition when the more conductive phase begins to form infinite clusters is clearly essential to an understanding of the system. It is these cases (insulating and conducting media) where percolation theory has the possibility of being most useful, and for this reason we shall



confine ourselves to examples of this type in the present section. We shall consider three types of problems, the first being introduced mainly for tutorial purposes. It suggests at first glance that there may exist a universal property which might be useful in solving a variety of other problems. We shall examine the validity of this idea. The second and third examples bear on some very real and potentially useful physical situations.

#### A. Close-packed mixtures of conducting and insulating spheres

In a recent paper Sher and Zallen<sup>19</sup> remarked that if conducting and insulating spheres (circles in 2D) of radii equal to half the nearest-neighbor separation were centered on the nodes of various 3D and 2D lattices, percolation of the conducting spheres always occurred when the volume (or area in 2D) fraction of these spheres  $\approx 0.15$  ( $\approx 0.44$  in 2D). They therefore made the reasonable suggestion that a *random* close-packed arrangement of the same conductive and insulating spheres (or circles), or perhaps a powder mixture<sup>20</sup> would percolate at this same volume (or area) fraction; this suggests the concept that these particular fractions represent invariant quantities which depend only on the dimensionality of the problem. It is evident that while the physical applications of this particular problem are not legion, the concept of a critical volume fraction (CVF), as Sher and Zallen define it, could be most useful. The CVF concept was critically examined in paper I from a mathematical viewpoint. Below we use the results of paper I to determine the usefulness of the CVF in solving real physical problems.

#### B. Conducting particles embedded in a continuous insulating medium

Examples of this case include commercially available products such as polymers loaded with silver particles used for flexible conductors and various conductive epoxies and adhesives. It should be noted at the outset that this case is, in principle, quite different from that of Sec. VA; here there is no hard-core property of the insulating phase which tends to promote contact among the conductive particles. In fact with no attractive interaction between the conductive regions (such as electrostatic forces) or with no packing forces (such as gravity) there is little reason to expect particle-to-particle contact. *A priori*, then, we would not expect percolation of the metallic phase to occur at Sher and Zallen's<sup>19</sup> critical volume fraction, although they have suggested<sup>19</sup> that this is indeed the case—citing unpublished data on one experimental mixture as verification.

We have examined several studies<sup>21-26</sup> of conduction in these types of systems and we find that there

is in general *no* particular volume fraction (except 1.0) which guarantees metallic conductivities. Values quoted in the published literature range from a CVF of 6%<sup>21,27</sup> up to 37%.<sup>23</sup> In fact, in several cases high conductivity in mixtures having  $V_c$  (for the conducting phase) considerably greater than 0.15 could be destroyed by applications of stress<sup>28</sup> indicating that the nature of the particle to particle contact was rather tenuous. Another study<sup>26</sup> showed that the conductivity of silver-loaded polymers depended drastically on the stirring time *after* the mixture had achieved apparent homogeneity. We have also performed two-dimensional computer studies of hard-core circles percolating in a continuous medium; the results of these studies reinforce the notion that the volume (area) fraction at percolation is not even approximately invariant (see Secs. V and VI of paper I). We are therefore forced to conclude that percolation of rigid or hard-core particles in a continuous medium is too complex a problem (particularly if a variety of shapes and sizes of particles and of preparation techniques is allowed) to lend itself to the simple approach suggested by Sher and Zallen.

#### C. Conduction in mixtures of continuous insulating and conducting media

This example is logically the final progression from Secs. VA and VB; here there is no longer any hard-core property of either phase, or equivalently no minimum size for regions of either constituent. One physical example of this might be an emulsive mixture of two immiscible liquids, one of which is conducting. A second and at present more relevant example originates from various attempts to characterize the so-called mobility edge in amorphous semiconductors. A simple characterization suggested by Ziman<sup>29</sup> and others<sup>30,31</sup> is to consider the movement of carriers in the classically allowed regions ( $E_{\text{electron}} > E_{\text{pot}}$ ) of the random one-electron potential characteristic of amorphous systems. The working hypothesis behind this picture is that the electronic states change from localized to extended in character at the energy  $E_c$  where the classically allowed regions form infinite clusters; a reasonably large jump in the carrier mobility would thus be expected at the energy characterizing this percolation threshold. Later experiments by Last and Thouless<sup>32</sup> using conductive paper and by Kirkpatrick<sup>7</sup> using resistor networks have suggested that this edge may be in effect softer than had been previously postulated: nevertheless the determination of  $E_c$ , the energy of this percolation edge, remains an important problem. We shall dwell only upon this aspect of the situation and ignore for the moment the questions that can be raised about the applicability of this somewhat simplistic model to real amorphous materials.

Zallen and Sher<sup>30</sup> have suggested that the critical volume fraction concept is relevant in this case and they have in fact calculated  $E_c$  on this basis for a number of reasonable random potential distributions. In view of the results discussed for Sec. VB and the variety of volume fractions at percolation listed in Table III of paper I (see also Appendix A of paper I) we tend to disagree. We suggest that the solution to these problems lies in the detailed topological characterization of each particular case rather than in a simple statistical quantity such as the volume fraction. Computer-based analyses of these situations appear tractable, and it would appear imperative that these (or other techniques) be carried out before any definitive statements can be made about the possible location of mobility edges.

## VI. CONCLUSIONS

Using improved computer iteration techniques, we have evaluated the conductivities of a large number of simple cubic and random-lattice conductance networks. The results show that a critical path analysis can be made to yield accurate predictions of the conductivity variation of these networks if the values of the approximately five to six largest conductances from each node are spread over at least seven to eight decades. We point out that these conditions are met in the Miller-Abrahams resistor network simulation of impurity conduction in lightly compensated semiconductors, and we deduce an accurate conductivity formula for this case.

Based on the conclusion in the previous paragraph, we have examined exact critical-path-percolation models for the two- and three-dimensional variable range hopping problems. Although no numerically exact solutions for these models are presented, we argue that on the basis of the percolation concepts and solutions discussed in paper I, a critical path analysis of these problems using a *simplified* form for the intersite impedances yields a precise  $T^{-1/3}$  or  $T^{-1/4}$  of  $\log\sigma$  in two and three dimensions, respectively, with values of  $C_2$  and  $C_3$  higher than those previously predicted. We then presented the computer calculated conductivities of a large number of resistor networks simulating this problem in three dimensions. From these data, we have deduced accurate empirical formulas for the dependence of  $\log\sigma$  on temperature, wave-function radius, and density of states. We note that these formulas are close to but not exactly in the  $T^{-1/4}$  form. We also give a formula for the two-dimensional variable-range hopping empirically deduced from several resistor networks simulating this problem.

On the basis of the results of paper I, several experimental studies of conduction in mixtures,

and our computer models simulating these problems, we have concluded that application of the critical volume fraction rule originally proposed by Scher and Zallen is appropriate only in rather limited circumstances. These cases include mixtures of two media each having hard-core properties (like powder mixtures) or mixtures in which one hard-core constituent in a deformable matrix is subjected to some type of packing force. In other situations, such as those appropriate to finding the so-called mobility edge energy of a collection of random potentials, specific account of the topological properties of the problem must be taken into account in finding the percolation threshold.

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## APPENDIX A

To illustrate the need for our cluster relaxation technique, we first describe the simplest standard relaxation procedure for solving conductance networks. Consider two adjacent nodes,  $A$  and  $B$ , in the network which are joined by a critical conductance  $G_{AB} = G_C$ . Let all nodes directly connected to  $A$  (including  $B$ ) be denoted by the index  $i$ , and likewise nodes to  $B$  by  $j$ . In the process of iteration towards the solution the network nodes will have, in general, voltages unequal to their final value. One iteration consists of adjusting the voltage of a node to make the excess current into that node equal to zero (to obey Kirchhoff's law). For example, the voltage of node  $A$  is incremented by

$$\delta V_A = -\delta I_A / \sum_i G_{Ai} , \quad (\text{A1})$$

where each  $G_{Ai}$  is a conductance directly connected to  $A$ , and the excess current into  $A$  is given by

$$\delta I_A = \sum_i V_{Ai} G_{Ai} . \quad (\text{A2})$$

From both of the above equations one can see that for large spreads in the conductance values ( $A > 10^3$ ), the excess currents and the consequent iterative voltage adjustments are controlled by the largest conductances into a given node. However, we know from Sec. II and particularly from Fig. 2 that the *final* currents are determined by the critical conductances. Hence also the voltage on either node of the critical conductance is determined by that conductance. Thus in the large spread regime the standard relaxation procedure in effect uses the "wrong" conductances to move toward the final solution. Because of this fact the

approach toward the final correct voltages is slowed drastically in the large- $A$  regime.

Our cluster relaxation procedure corrected for this by grouping together (every 20th iteration) all nodes which were connected to one another and which had the same voltage (within some small tolerance). Each cluster was then treated as a single node in the standard relaxation procedure. That is, the excess current flowing into the cluster was computed and then the voltage of each node in the cluster was incremented by the same amount to cause the excess current into the cluster to be zero. In practice it was found beneficial to make the cluster-definition voltage tolerance smaller as convergence was approached.

#### APPENDIX B

Imagine a uniform linear spatial expansion of all  $x-y$  distances in Fig. 5 by a factor  $f$ . Thus all points  $i$  and  $j$  in the expanded space have  $\Delta x_{ij}$  and  $\Delta y_{ij}$  enhanced by the factor  $f$  but  $\Delta E_{ij}$  unchanged. At the same time expand the radius of each IF figure by the same factor  $f$ , but leave its height unchanged. If these figures were just percolating before the transformation they will also be *just* percolating after, for all the points that were bonded before the transformation will be bonded afterwards. These new figures, however, correspond to those drawn about the points which are now arranged with a density  $N' = N/f^2$  at temperature  $T' = T/f$ , where  $T$  was the temperature corresponding to the original figures. Since  $E_{\max}$ , the height of

the figures, is unchanged, the new critical value of  $\xi$  for these figures is  $\xi'_c \equiv (E_{\max}/kT') = (fE_{\max}/kT) = f\xi_c$ . We have thus shown that

$$\xi_c(N', T') = f\xi_c(N, T), \quad (B1)$$

where  $N' = N/f^2$  and  $T' = T/f$ . We now can make a second, different expansion of *all* the coordinates ( $X$ ,  $Y$ , and  $E$ , this time) of the points and shells in Fig. 5 by a factor  $\gamma$ . Again we have the result that if the figures were just percolating before the expansion, they will be just percolating after it. These new figures however correspond to those drawn about the points at the same temperature  $T$  but at the new density  $N' = \gamma^{-3}N$ . We have then

$$\gamma\xi_c(T, N) = \xi_c(T, \gamma^{-3}N). \quad (B2)$$

If we now agree to write

$$\xi_c(N, T) = C_2(N, T)/(a^2 N k T)^{1/3}, \quad (B3)$$

Eq. (B2) becomes

$$C_2(N, T) = C_2(N\gamma^{-3}, T) \quad (B4)$$

and Eq. (B1) becomes

$$C_2(N/f^2, T/f) = C_2(N, T) \quad (B5)$$

for all  $\gamma$  and  $f$ .

It is clear that these equations can *only* hold if  $C_2$  is not a function of either  $N$  or  $T$ , thus proving that percolation of these figures occurs at a constant number of bonds per site. A similar conclusion is readily reached for the 3D variable range hopping problem by considering the appropriate figures in 4-space.

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<sup>2</sup>Preliminary results have been given; see C. H. Seager and G. E. Pike, Bull. Am. Phys. Soc. **18**, 307 (1973); and G. E. Pike and C. H. Seager, *ibid.* **18**, 307 (1973).

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<sup>9</sup>For this case as well as for the random node resistor networks discussed later, we investigated the effect of varying the network size. It was generally observed that samples of 1000 nodes appeared to be large enough to yield answers reasonably representative of true macroscopic materials.

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<sup>11</sup>V. Ambegaokar, S. Cochran, and J. Kurkijärvi, Phys. Rev. B **8**, 3682 (1973). These authors have recently also made calculations of the conductivity of a random lattice of nodes interconnected by conductances determined by Eq. (1). They solve only a very few computer samples for  $N_s = 1000$  or greater. Also they could only solve the networks for values of  $2\bar{r}_s/a \leq 14.3$ , with our cluster iteration technique we could accurately solve models out to  $2\bar{r}_s/a = 26$ . Their results are in fairly good agreement with ours considering the difficulty they experienced with convergence at large values of  $2\bar{r}_s/a$ .

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<sup>14</sup>M. L. Knotek, M. Pollak, J. M. Donovan, and H. Kurtzmann, Phys. Rev. Lett. **30**, 853 (1973).

<sup>15</sup>In this case as well as the  $R$ -percolation case, we believe that the appropriate average is the geometric average of the conductivities of our samples. To estimate the uncertainty in the mean (or most probable) value of the conductance at each temperature and state density we use the standard error of the mean,  $\sigma_m = \sigma/N^{1/2}$ , where  $\sigma$  is the standard deviation of the collection of  $N$  conductance values. Although this formula is only strictly correct for large  $N$ , it provides us with a rea-

sonable approximation to our errors in the present case. The uncertainty in the slopes of the lines in Fig. 6(a) is determined by constructing the lines of maximum and minimum tangent which cross at least 2/3 (~one standard deviation) of the individual point error bars. Since the errors were much smaller at higher temperatures, the values of the slopes were largely determined by the values of the conductances above 0.5 K. As is noted in the figure caption, the symbols about each point in Fig. 6(a) are considerably larger than the actual estimated errors.

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states which are at least several  $kT$  from  $E_f$ , the use of the Boltzmann approximation appears to be a justifiable simplification and in our opinion should cause no serious errors.

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